

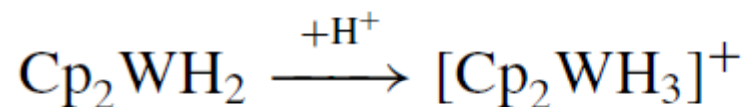
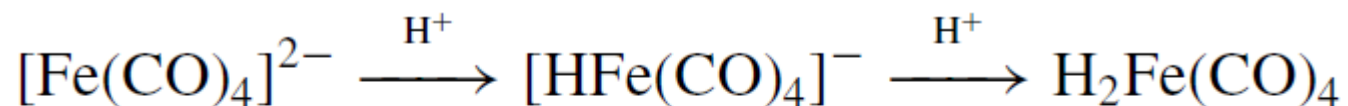
Metal Hydride Complexes

- Main group metal hydrides play an important role as reducing agents (e.g. LiH, NaH, LiAlH_4 , LiBH_4).
- The transition metal M-H bond can undergo insertion with a wide variety of unsaturated compounds to give stable species or reaction intermediates containing M-C bonds
- They are not only synthetically useful but are extremely important intermediates in a number of catalytic cycles and also in battery technologies.

Transition Metal Hydride Preparation

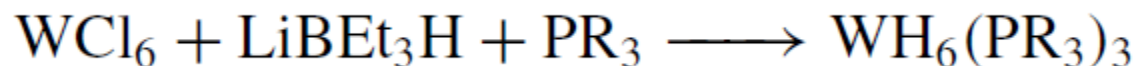
1. Protonation

- requires an electron rich basic metal center



1. From Hydride donors

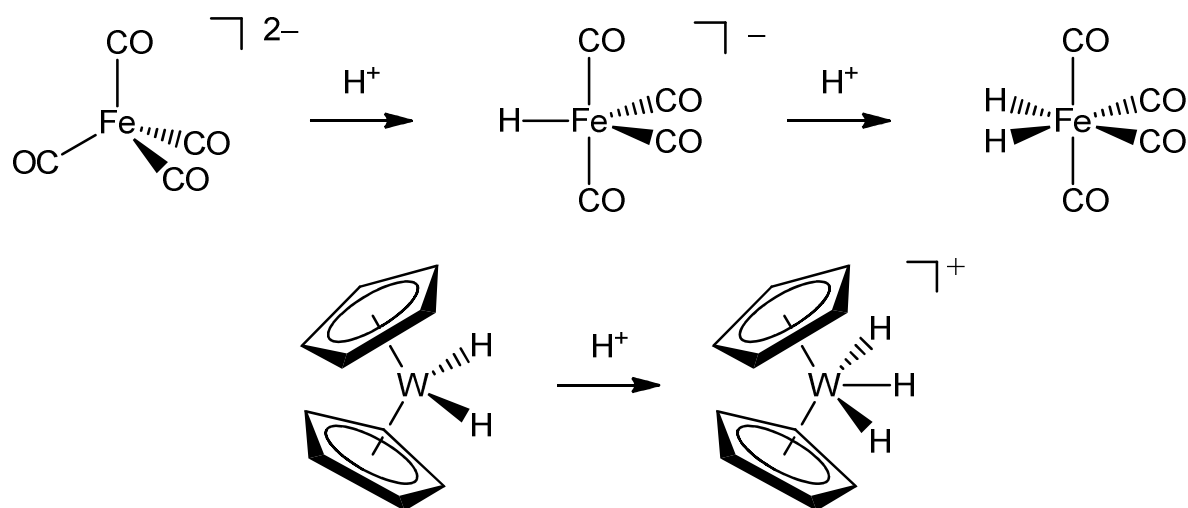
- main group metal hydrides are typically used as donors.



Transition Metal Hydride Preparation

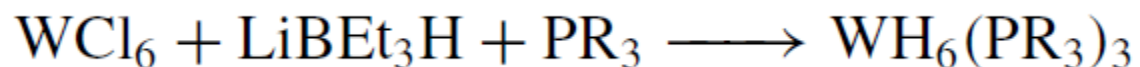
1. Protonation

- requires an electron rich basic metal center



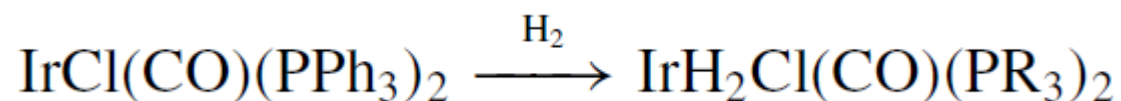
2. From Hydride donors

- main group metal hydrides are typically used as donors.

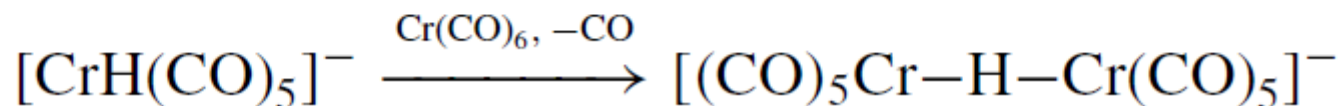
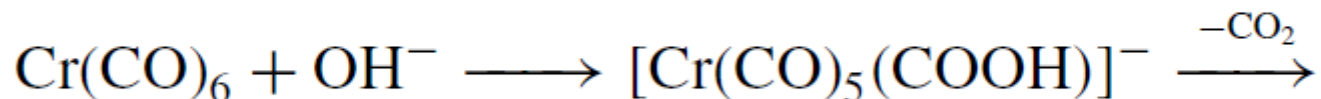
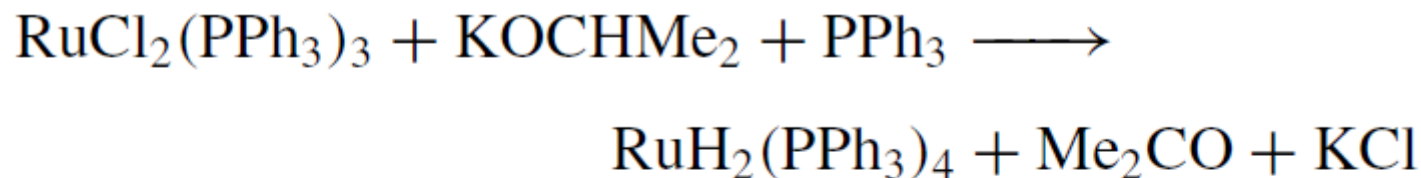


3. From H₂

- via oxidative addition
- requires a coordinatively unsaturated metal center

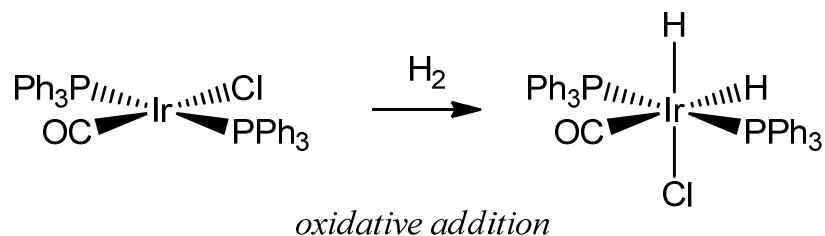


3. From a ligand (β-elimination)

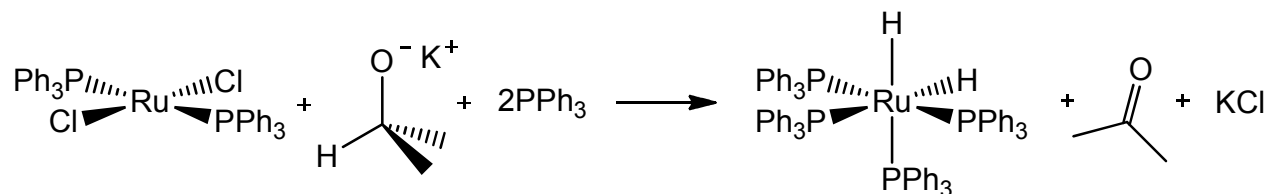


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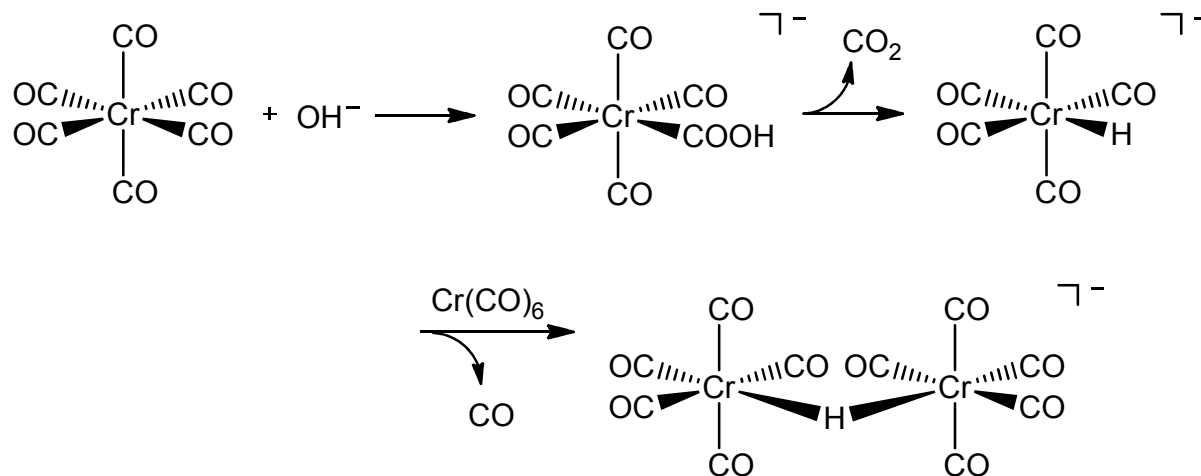
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3. From a ligand (β-elimination)

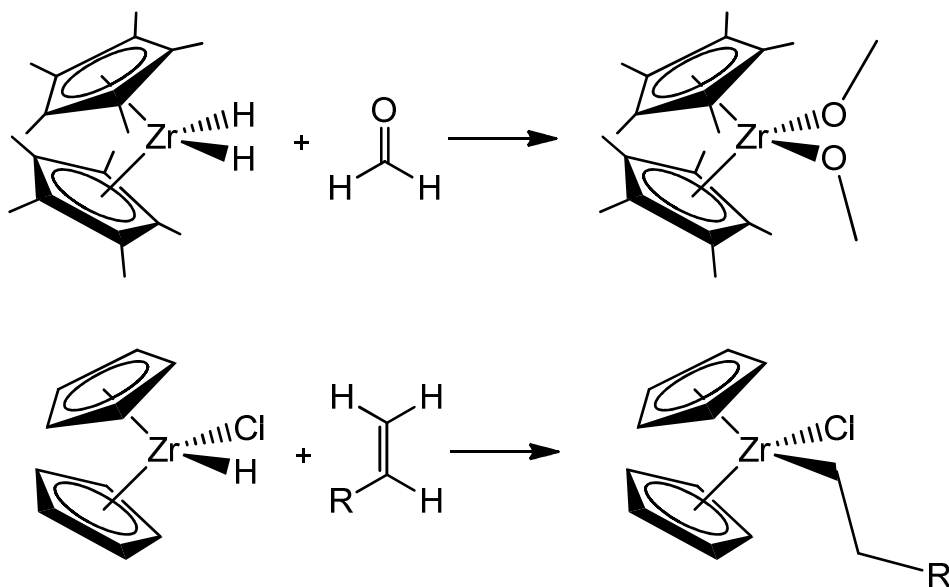


4. From a ligand (decarboxylation)



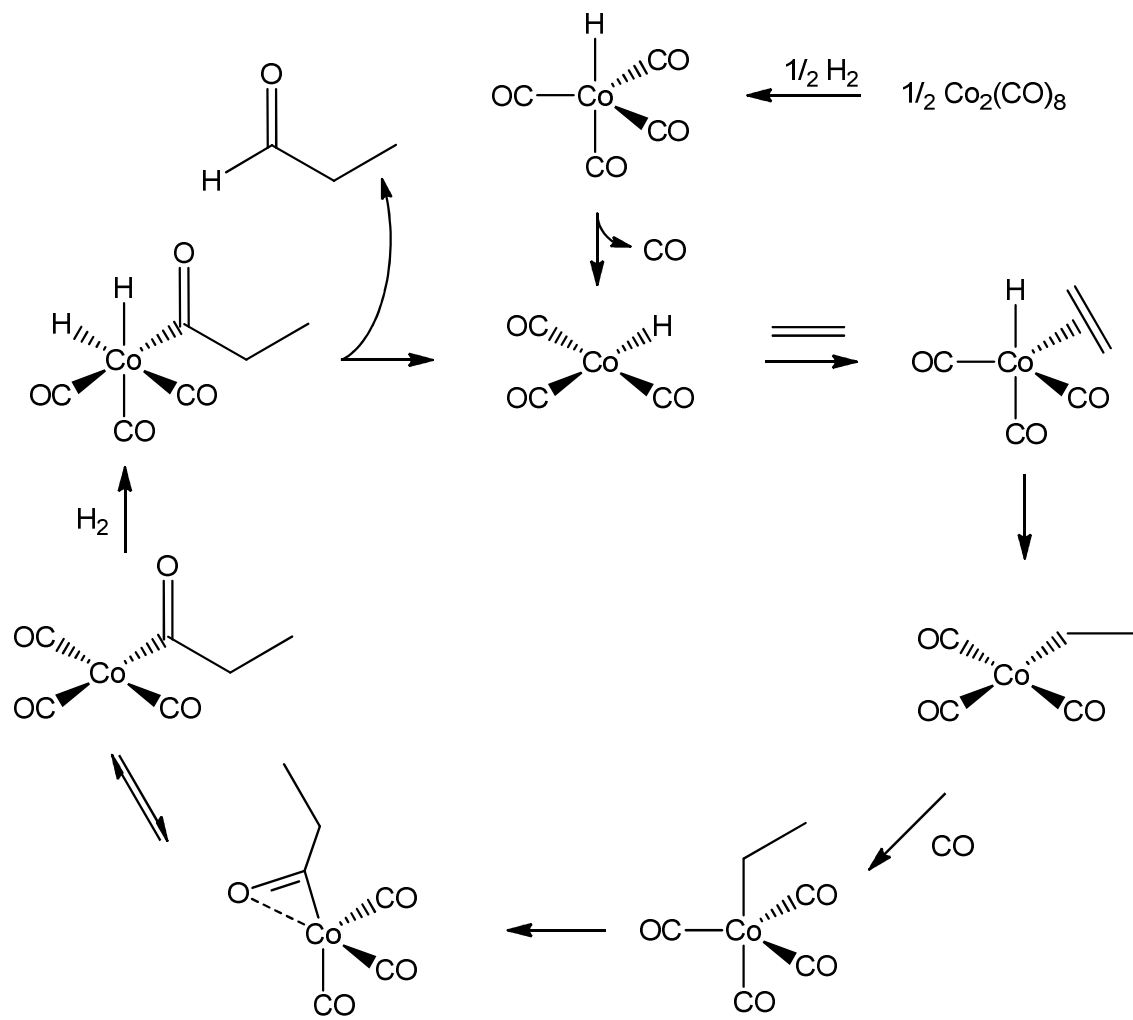
Transition Metal Hydride Reactivity

- Hydride transfer and insertion are closely related

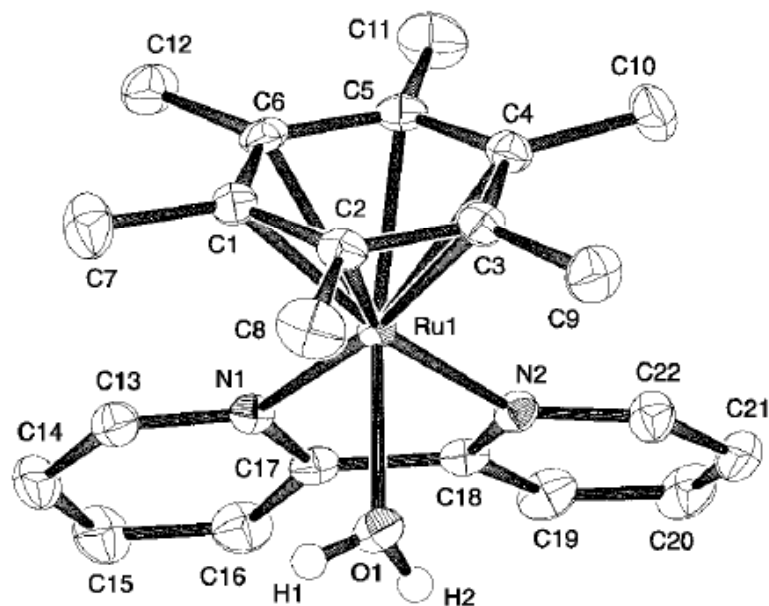
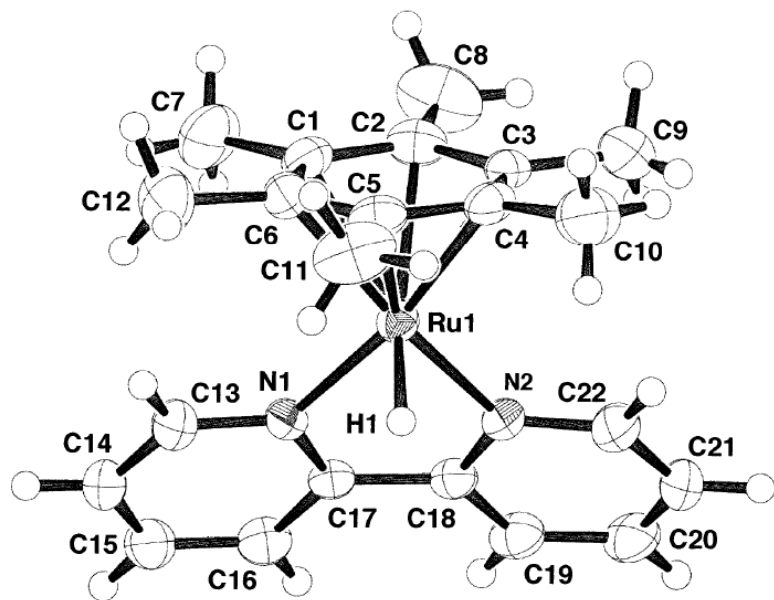


- A metal hydride may have acidic or basic character depending on the electronic nature of the metal involved (and of course its ligand set).
- Early transition metal hydrides tend to carry significant negative charge on the H atom whereas later more electronegative transition metals favour a more positive charge on the H atom (the term Hydride should therefore not be taken literally).
- Reactivity can also depend upon the substrate, e.g. CpW(CO)₃H is a H⁺ donor to simple bases, a H[•] donor toward styrene and a H⁻ donor to carbonium ions.

- $\text{HCo}(\text{CO})_4$ is a strong acid ($\text{pK}_a \sim 8.5$) due to the electron withdrawing effect of the σ -donating, π -accepting CO ligands on the Co(I) center. It is commonly used as a hydroformylation catalyst.

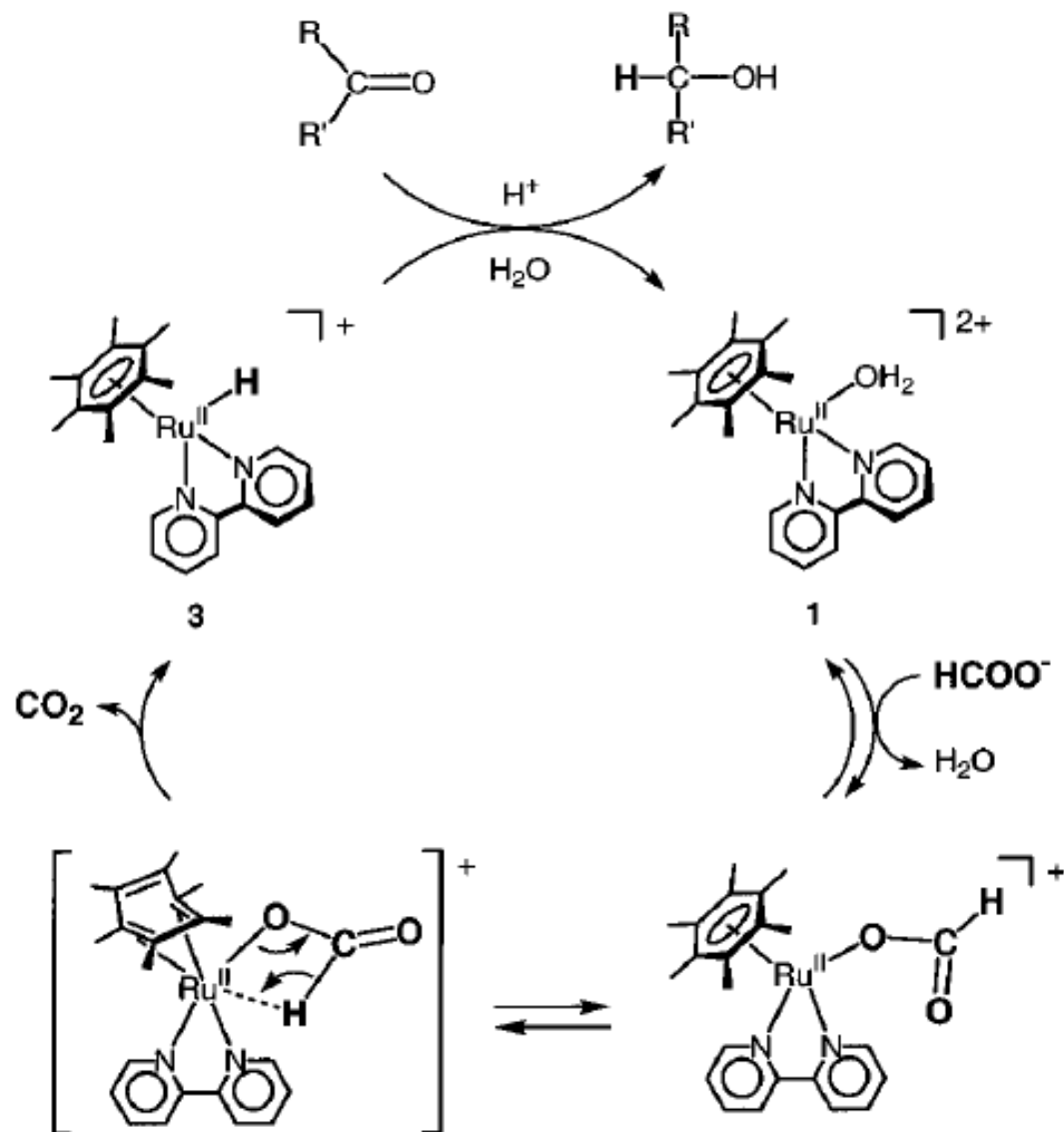


- An example of an isolable late transition metal hydride complex $[(\eta^6\text{-hmb})\text{Ru}^{\text{II}}\text{Hbpy}]^+$ and its aqua derivative $[(\eta^6\text{-hmb})\text{Ru}^{\text{II}}(\text{OH}_2)\text{bpy}]^{2+}$ (hmb = hexamethylbenzene)

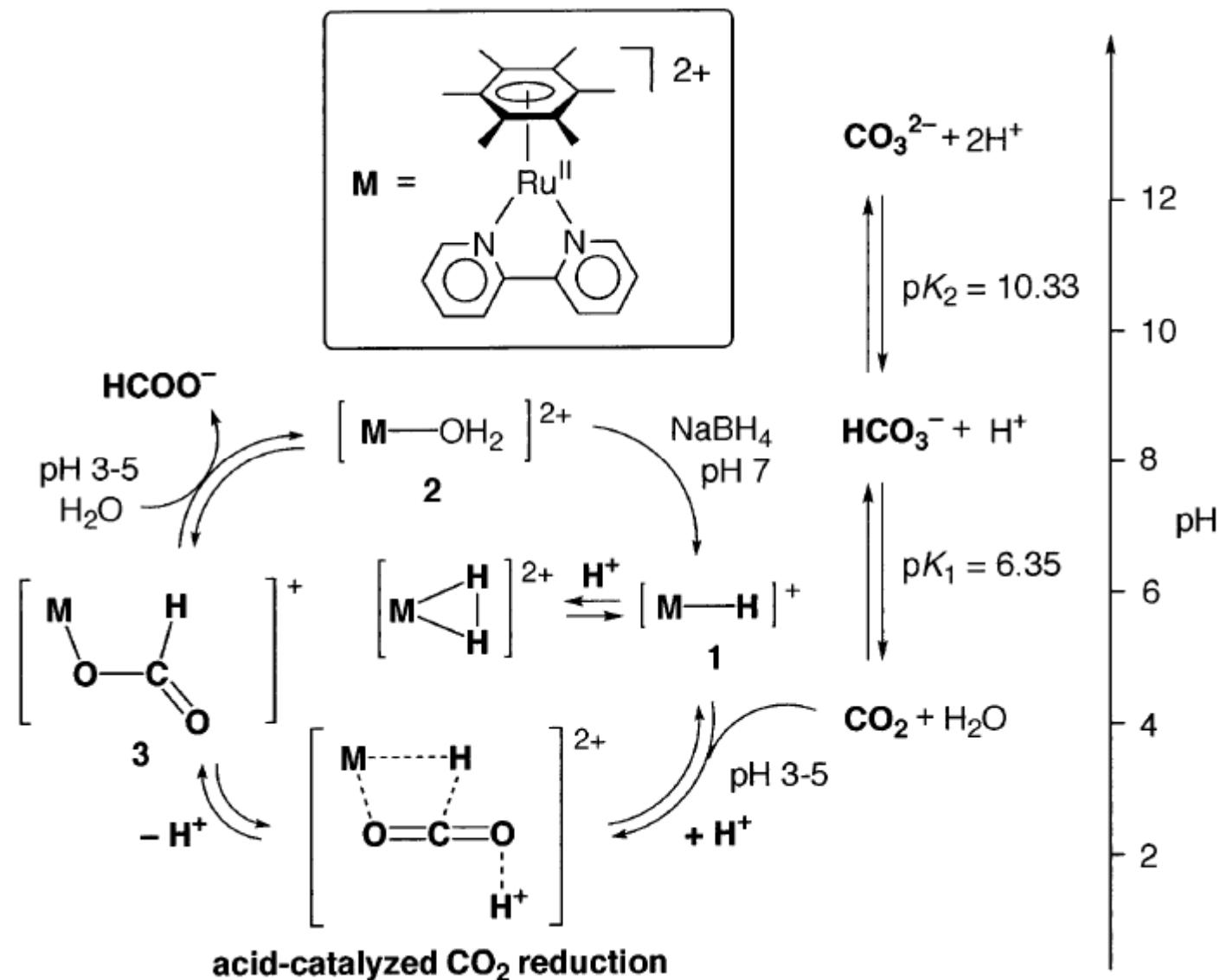


Hayashi et al. J. Am. Chem. Soc., 2003, 125 (47), 14266-14267
 Ogo et al. Organometallics, 2002, 21 (14), 2964-2969

- Applied in catalysis to promote ketone reduction e.g. acetone to isopropanol. The formate ion (HCO_2^-) is used as a source of H^- with liberation of CO_2 .

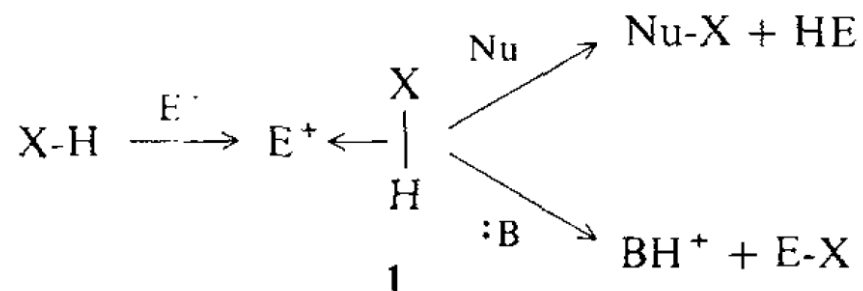


- The same catalyst can be used for reduction of CO_2 under the appropriate conditions.

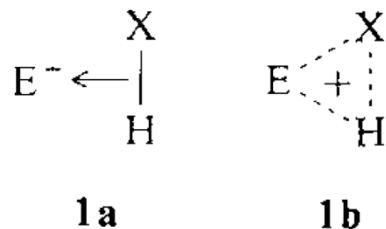


Dihydrogen σ -complexes

- An electrophile E^+ can react with an X-H bond to give a **σ complex 1**, in which the X-H bond acts as a 2e donor. (*not to be confused with σ -bonding Hydrides*)

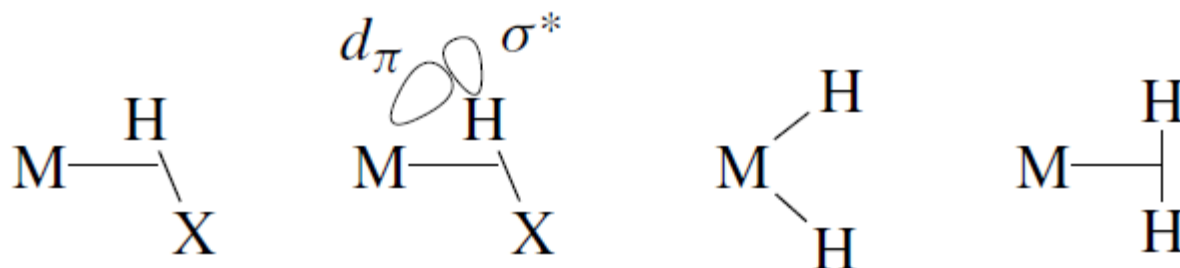


- 1 a** and **1 b** show two common ways of representing **1**. Coordination to E^+ alters the chemical properties of the X-H bond and can activate it either for nucleophilic attack at X or deprotonation.

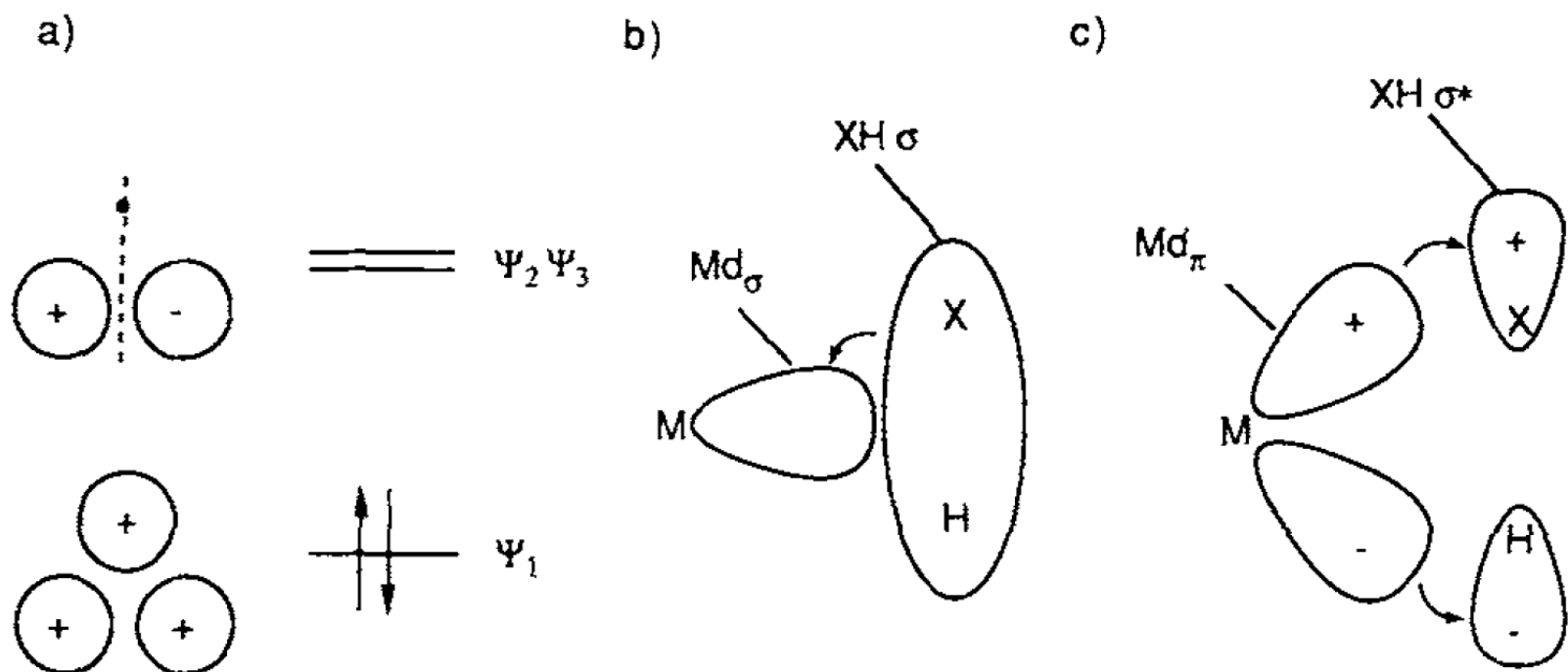


- The X-H bond is always coordinated side-on to E^+ , as in **1**.

- ***σ complexes*** bind by donation of the X-H σ -bonding electrons in a 2e 3 center bond to the metal.



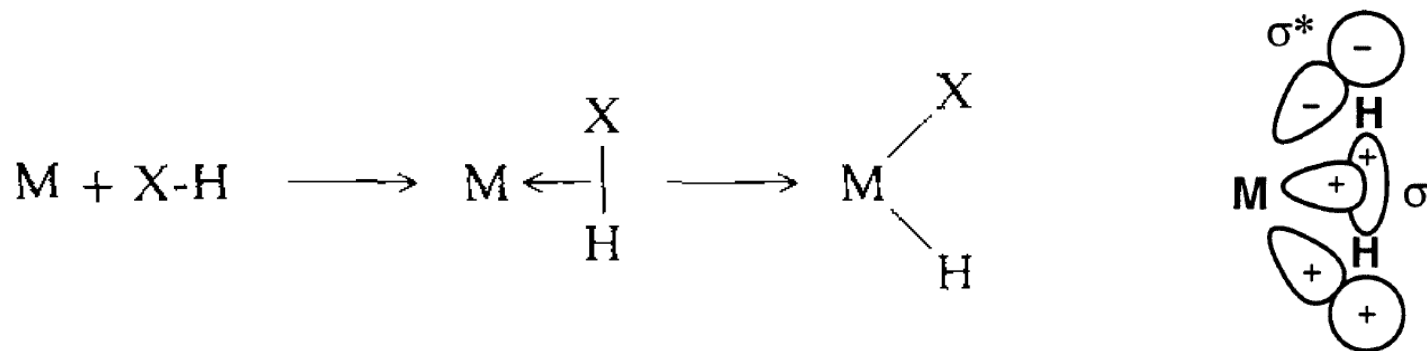
- X = H, Si, Sn, B, or P.....***at least one H must always be present.***
- The H atom has a small atomic radius and carries no lone pairs or other substituent's, allowing the hydrogen end of the X-H bond to approach close to the metal and so allow the filled M $d\pi$ orbital to back-bond relatively strongly onto the lobe of the X-H σ^* orbital that is located on the H atom.



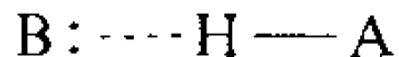
- **The bonding picture for a σ complex.**

- Only the Ψ_1 orbital which bonds over all three centers, is occupied. Occupation of Ψ_2 would lead to the opening of one edge of the triangle (nodal plane marked as a dotted line).
- In an M-(H-X) complex the electrons of the X-H σ bond are donated to an empty metal d, orbital. This is analogous to the binding of the lone pair on NH_3 to a metal atom.
- Electron density from the M($d\pi$) orbital is donated to the X-H σ^* orbital (back-donation). This resembles M($d\pi$) + CO(π^*) back-donation and is unique to transition metal σ complexes.

- An isolable complex must have some backbonding, but **strong back-donation leads to cleavage of the X-H bond by oxidative addition to give an X-M-H complex.**

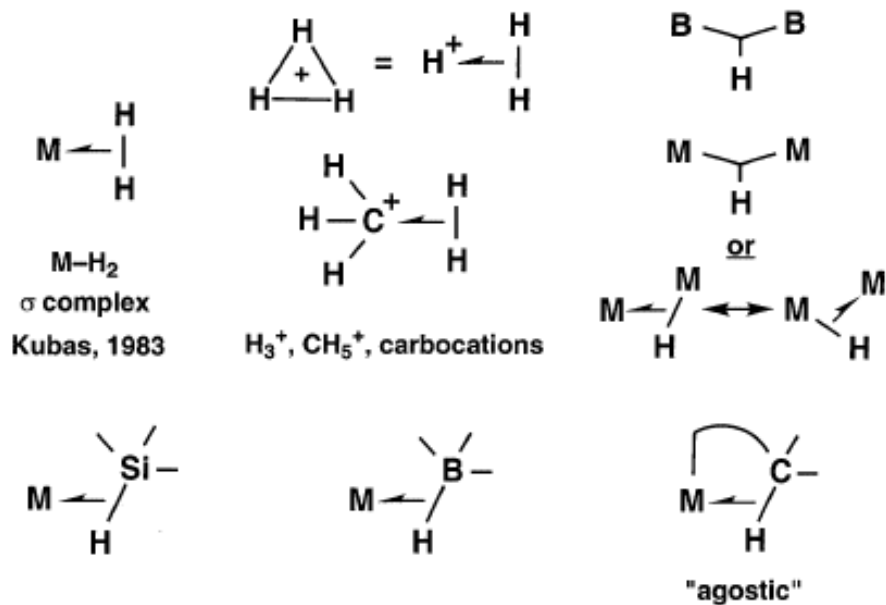


- In contrast, below is a four-electron system, where Ψ_2 must be filled. As this molecular orbital has an antibonding interaction on one side of the triangle, formation of a linear structure is preferred.



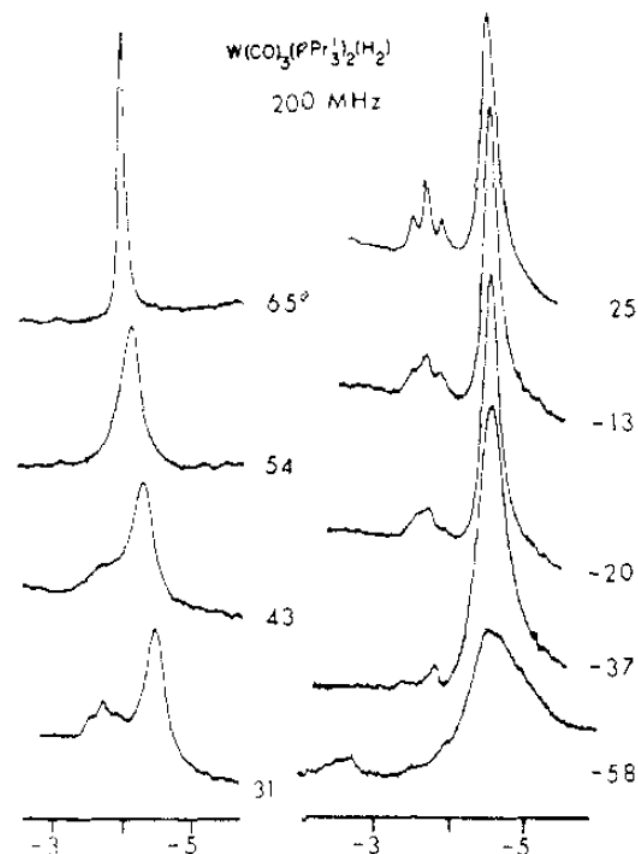
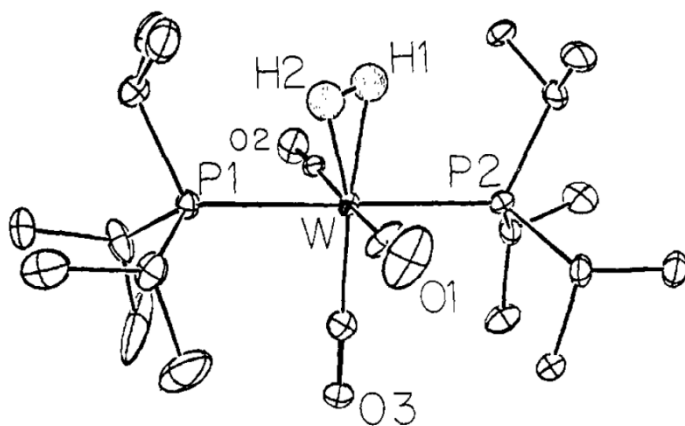
- In complexes with weak back-bonding, the length of X-H bond is similar to that in free X-H.
- The acidity and electrophilicity of X-H can be strongly enhanced, however, because ***σ bonding reduces the electron density in the X-H unit.***
- Stronger back-donation can lead to σ complexes with elongated X-H bonds and reduced electrophilicity of the X-H group.

NONCLASSICAL 3-CENTER, 2-ELECTRON (3c-2e) BONDS



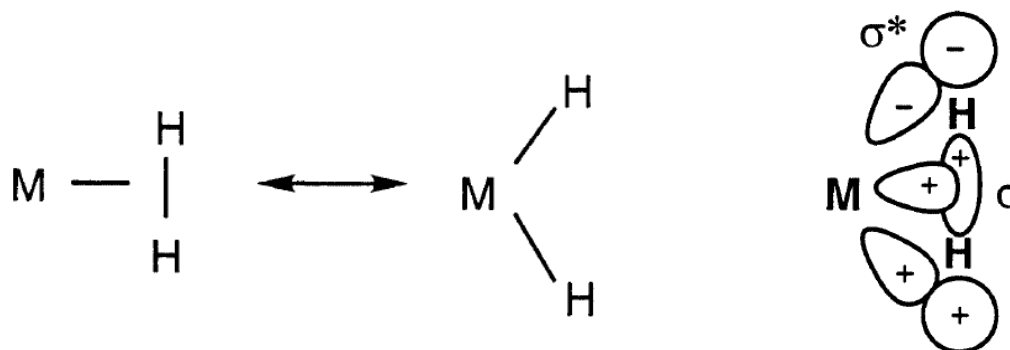
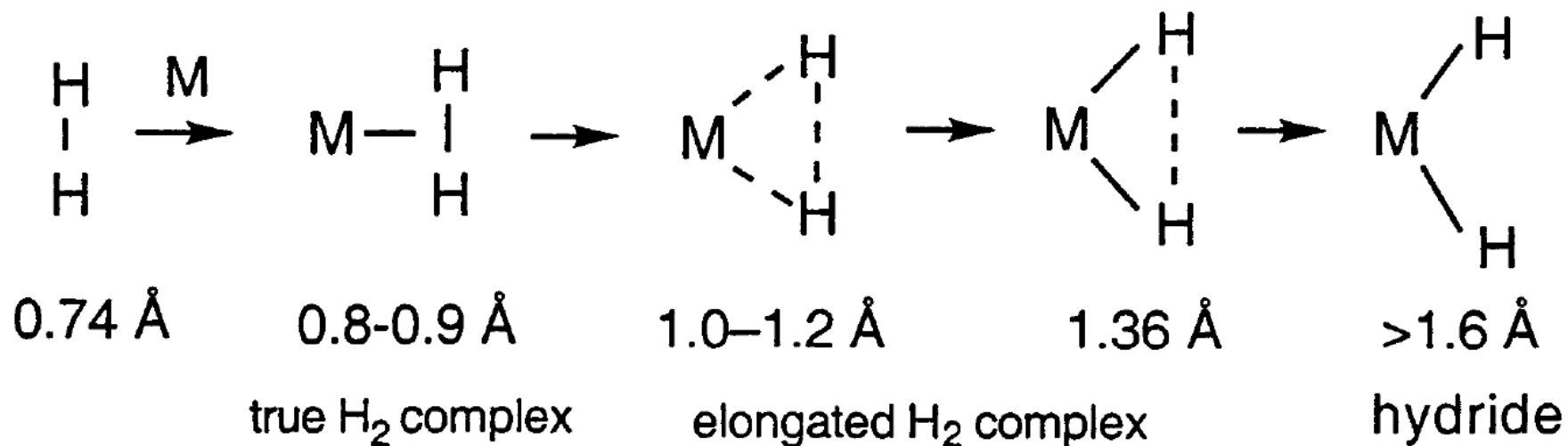
Characterization Criteria for Dihydrogen Coordination

- Dihydrogen complexes have been characterized by X-ray, or, much better, neutron diffraction.
- An IR absorption at 2300–2900 cm^{-1} is assigned to the H–H stretch, but it is not always seen.
- The H_2 resonance appears in the range 0 to -10δ in the ^1H NMR and is often broad.
- The presence of an H–H(D) bond is shown by the H,D coupling constant of 20–34 Hz in the ^1H NMR spectrum of the H–D analog. This compares with a value of 43 Hz for free HD and ~ 1 Hz for classical H–M–D species.
- Coupling to ^{31}P or the metal center normally is not resolved, even at low temperature.
- J_{HD} is often unobservable in fluxional complexes that also contain hydrides.
- Crabtree developed a second criterion: proton relaxation time
- T_1 was anticipated to be unusually short (4–100 ms) for H_2 ligands vs > 350 ms for hydrides.

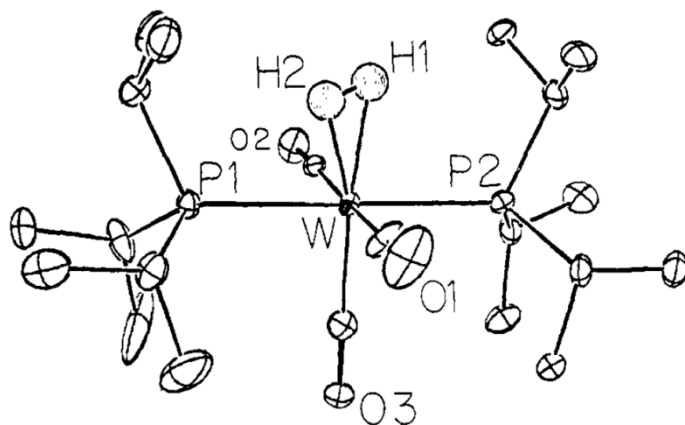


- In prototypical dihydrogen complexes, there are a number of cases where both 6-coordinate dihydrogen and 7-coordinate dihydride structures are reported to exist in dynamic equilibrium, indicating a delicate energetic balance between two quite different structures.
- For example, NMR observations establish that the **dihydrogen** complex $(\text{PCy}_3)_2\text{W}(\text{CO})_3(\text{H}_2)$ is in equilibrium with the **7-coordinate dihydride complex** $(\text{PCy}_3)_2\text{W}(\text{CO})_3\text{H}_2$, with the dihydrogen form predominant.

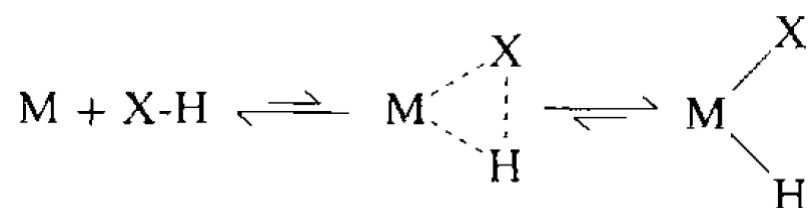
H-H BOND DISTANCES FROM CRYSTALLOGRAPHY AND NMR



- The H-H distance of 0.82 Å observed by neutron diffraction is little changed from its value in free H₂ (0.74 Å).
- Since the H-H bonds in most H₂ complexes are not stretched, it is not surprising that the activation energy for loss of H₂ (more generally X-H) is not usually large.
- Facile loss of X-H can be important in applications to catalysis, for example, because the resulting coordinatively unsaturated intermediates may be very reactive.

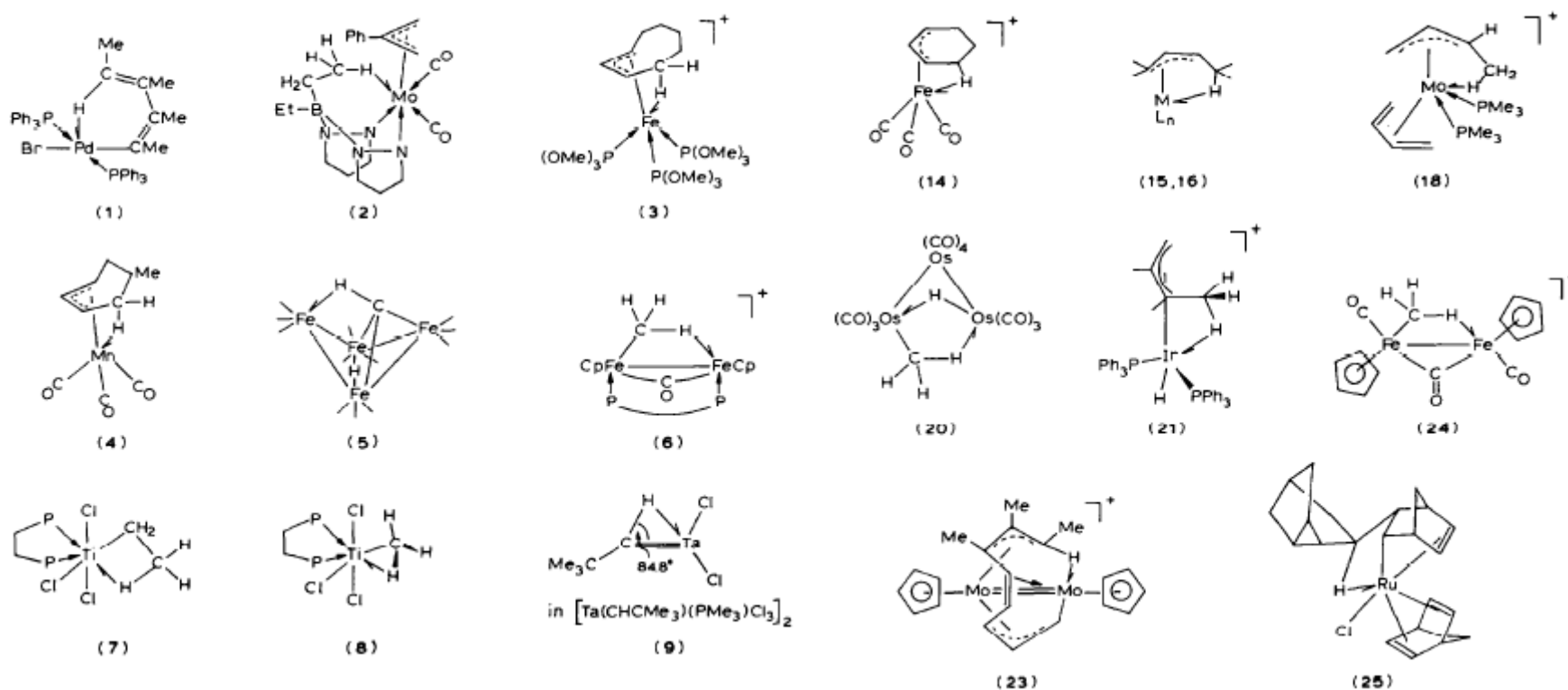


- We can also look at σ complexes as being derived from the classical adduct $[L_nM(X)(H)]$ in which an attractive interaction between X and H causes these two ligands to approach one another.
- This description is more appropriate for "stretched" σ complexes in which the X-H distance is substantially longer than in the free XH molecule.



- Eisenstein et al. have shown how hydrido ligands even in classical dihydrides of type $[L_nMH_2]$ have a mutually attractive interaction not present in CH_4
- Attractive interactions between ligands are likely to facilitate reactions such as reductive elimination and insertion - reactions in which two ligands must approach each other to reach the transition state.
- ***By stabilizing the transition state for oxidative addition and reductive elimination the activation energy is thus lowered.*** This helps explain the special facility of these reactions in transition metal complexes.

- Starting in the early 1980s, the activity in the area of C-H activation led to renewed interest in compounds with C-H-M bridges.
- In their 1983 review, Brookhart and Green directed attention to C-H-M systems, which they named agostic.

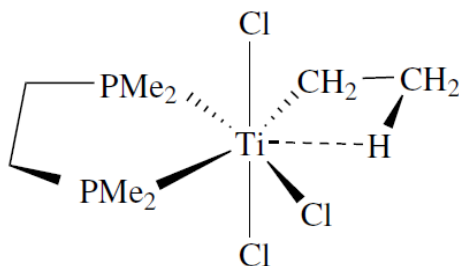


Journal of Organometallic Chemistry, 250 (1983) 395-408

“We propose the term “agostic” which will be used to discuss the various manifestations of covalent interactions between carbon-hydrogen groups and transition metal centres in organometallic compounds. The word agostic will be used to refer specifically to situations in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and to a transition metal atom.”

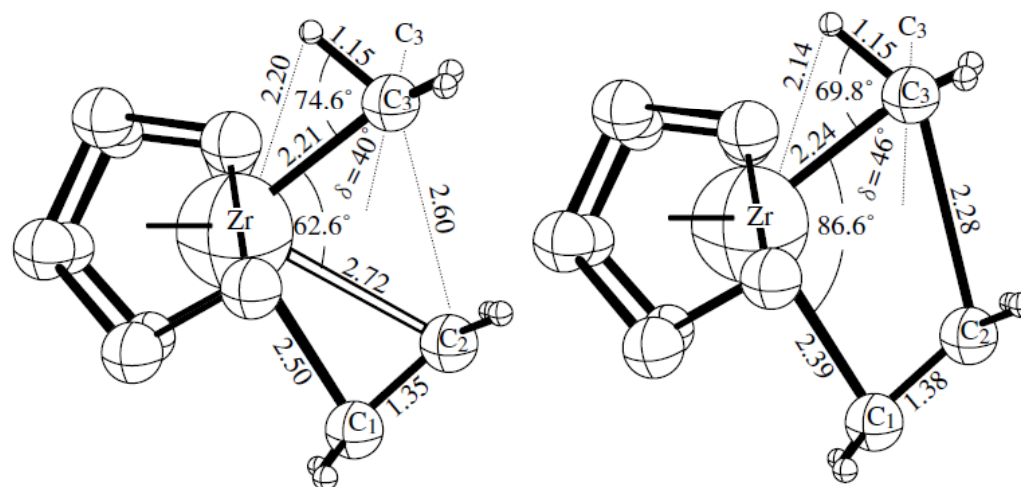
Agostic Bonds

- The β C–H bond is bound to the metal in a way that suggests that the alkyl is beginning the approach to the transition state for β elimination.
- These agostic alkyls can be detected by X-ray or neutron crystal structural work and by the high-field shift of the agostic H in the proton NMR.
- The lowering of the $J(\text{C,H})$ and $\nu(\text{CH})$ in the NMR and IR spectra, respectively, on binding is symptomatic of the reduced C–H bond order in the agostic system.



- The reason that β elimination does not occur is that the d^0 Ti has no electron density to back donate into the σ^* orbital of the C–H bond.
- This back donation breaks the C–H bond in the β -elimination reaction, much as happens in oxidative addition.

- Agostic binding of C–H bonds also provides a way to stabilize coordinatively unsaturated species.
- They are also found in transition states for reactions such as alkene insertion/ β elimination either by experiment or in theoretical work.



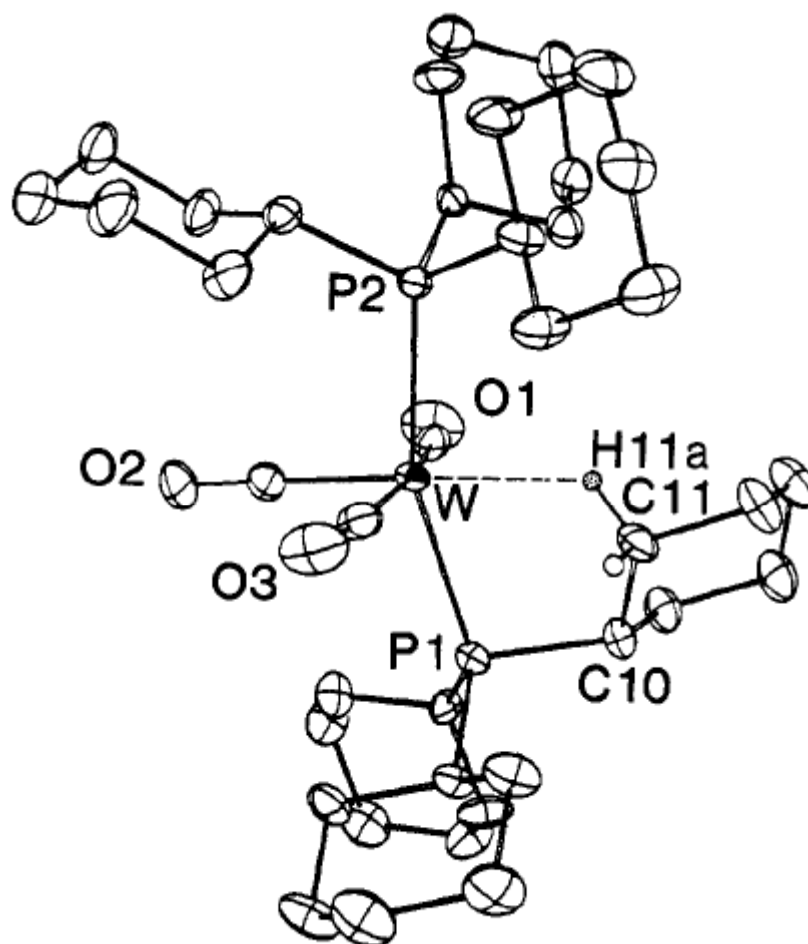


Figure 2. Ortep drawing of $\text{W(CO)}_3(\text{PCy}_3)_2$ (30% thermal ellipsoids).